Standard Operating Procedure for the Analysis of PCBs and Organochlorine Pesticides by GC-ECD

Karen Harlin, Kaye Surratt, and Cathy Peters
Illinois State Water Survey
Office of Atmospheric Chemistry
2204 Griffith Drive
Champaign, IL 61820

Standard Operating Procedure CH-IN-002.3

November 1995

Revision 3.0

Acknowledgments

The authors wish to acknowledge the contributions of Monte Wilcoxon in the generation of chromatograms and data tables for this SOP.

Standard Operating Procedure for the Analysis of PCBs and Organochlorine Pesticides by GC-ECD

1.0 Scope and Application

This procedure details the analysis and data reduction methods utilized to determine polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCs) in vapor, particulate, and precipitation samples. The method is specific to the Lake Michigan Mass Balance (LMMB) and Lake Michigan Loading Study (LMLS) projects. The following analytes are measured by this SOP using gas chromatograph-electron capture detection methods:

Polychlorinated Biphenyls (PCBs)-Total and 105 congener peaks

congener (BZ)	CAS #
1	2051-60-7
3	2051-62-9
4+10	13029-08-8, 33146-45-1
6	25569-80-6
7+9	33284-50-3, 34883-39-1
8+5	34883-43-7, 16605-91-7
12	2974-92-7
13	2974-90-5
15+17	2050-68-2, 37680-66-3
16	38444-78-9
18	37680-65-2
19	38444-73-4
21	55702-46-0
22	38444-85-8
24	55702-45-9
27	38444-76-7
25	55712-37-3
26	38444-81-4
29	15862-07-4
31+28	16606-02-3, 7012-37-5
32	38444-77-8
33	38444-86-9
37	38444-90-5

congener (BZ)	CAS #
40	8444-93-8
41+71	52663-59-9, 41464-46-4
42	36559-22-5
43	70362-46-8
44	41464-39-5
45	70362-45-7
46	41464-47-5
47	2437-79-8
48	70362-47-9
49	41464-40-8
51	68194-04-7
52	35693-99-3
53	41464-41-9
56+60	41464-43-1, 33025-41-1
63	74472-34-7
64	52663-58-8
66	32598-10-0
70+76	32598-11-1, 70362-48-0
74	32690-93-0
77	32598-13-3
81	70362-50-4
82	52663-62-4
83	60145-20-2
85	65510-45-4
87	38380-02-8
89	73575-57-2
91	68194-05-8
92+84	52663-61-3, 52663-60-2
95	38379-99-6
97	41464-51-1
99	38380-01-7
100	39485-83-1
101	37680-73-2
107	70424-68-9
110	38380-03-9
114+131	74472-37-0, 61798-70-7

congener (BZ)	CAS #
118	31508-00-6
119	56558-17-9
123+149	65510-44-3, 38380-04-0
128	38380-07-3
129	55215-18-4
130	52663-66-8
132+153+105	38380-05-1, 35065-27-1, 32598-14-4
134	52704-70-8
135+144	52744-13-5, 68194-14-9
136	38411-22-2
137+176	35694-06-5, 52663-65-7
141	52712-04-6
146	51908-16-8
151	52663-63-5
156	38380-08-4
157+200	69782-90-7, 52663-73-7
158	74472-42-7
163+138	74472-44-9, 35065-28-2
167	52663-72-6
170+190	35065-30-6, 41411-64-7
172	52663-74-8
173	68194-16-1
174	38411-25-5
175	40186-70-7
177	52663-70-4
178	52663-67-9
180	35065-29-3
183	52663-69-1
185	52712-05-7
187+182	52668-68-0, 60145-23-5
189	39635-31-9
191	74472-50-7
193	69782-91-8
194	35694-08-7
197	33091-17-7

congener (BZ)	CAS #
198	68194-17-2
199	52663-75-9
201	40186-71-8
202+171	2136-99-4, 52663-71-5
196	42740-50-1
203	52663-76-0
205	4472-53-0
206	40186-72-9
207	52663-79-3
208+195	52663-77-1, 52663-78-2
209	2051-24-3

Pesticides	CAS #
dieldrin	60-57-1
a-chlordane	5103-71-9
g-chlordane	5103-74-2
t-nonachlor	39765-80-5
a-hexachlorocyclohexane (a-HCH)	319-84-6
g-hexachlorocyclohexane (g-HCH)	58-89-9
hexachlorobenzene (HCB)	118-74-1
p'p'-DDD	72-54-8
p,p'-DDE	72-55-9
p,p'-DDT	50-29-3

2.0 Summary of Method

This method describes equipment and procedures for performing gas chromatographic analysis with an electron capture detector (GC-ECD). It includes instrument optimization specific for PCBs and OCs and data reduction.

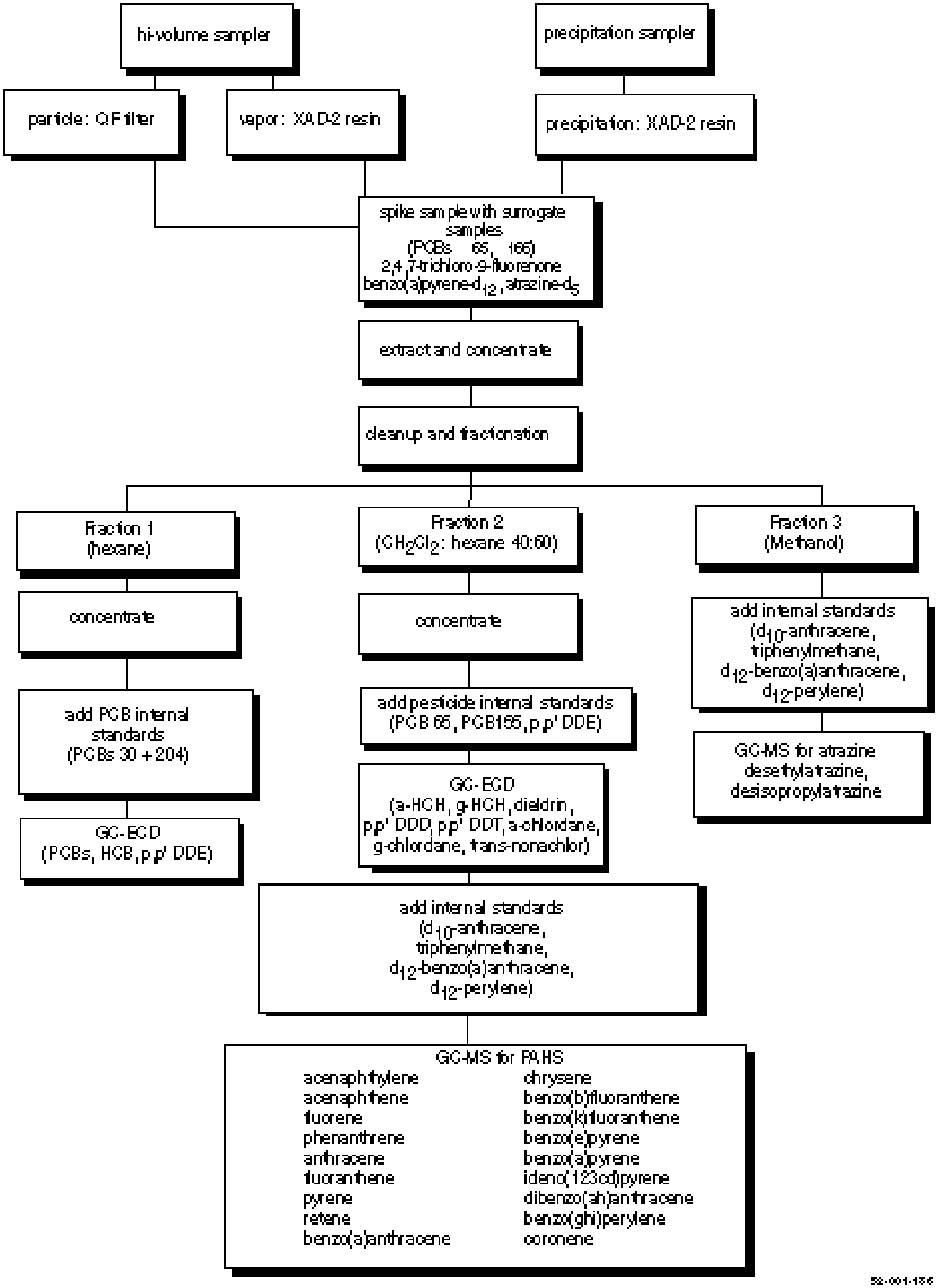
2.1 Personnel Restrictions

This method is restricted to use by or under the supervision of an analyst trained and experienced in the operation of gas chromatographs, electron capture detectors, and capillary chromatogram interpretation, and data reduction. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.2 Working Linear Range

A multi point calibration curve will be constructed for each analyte to document the working linear range.

2.3 Method Flow Diagram



3.0 Definitions

3.1 Limits of Detection

3.1.1 Instrument detection limit

The instrument detection limit (IDL) refers to the smallest signal above background noise that an instrument can reliably detect. The IDL is determined from a data set comprised of three separate chromatographic runs of a low level calibration standard; each run contains 7-10 analyses of the standard. The IDL equals the Student's t value (n-1) multiplied by the standard deviation of this data set.

3.1.2 Method detection limit

Method detection limits (MDL) are defined in CFR, Vol 49, No. 209, October 26, 1984, Appendix B to Part 136. Matrix specific MDLs are determined by spiking 7-10 clean matrix samples with the analytes of interest and processing them through the entire extraction, cleanup, and analysis procedure.

3.2 Internal standard (ISTD)

A pure analyte(s) added to a sample extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution.

3.3 Laboratory surrogate spike (LSS)

A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the LSS is to monitor method performance with each sample.

3.4 All other terms are defined in the QAPjP, Revision 5, July 1995.

4.0 Interferences

Method interferences may be caused by contaminants in solvents, the sampling matrix, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in gas chromatograms. Laboratory equipment and reagents will be monitored by the inclusion of quality control samples with each batch of samples prepared. Individual samples may contain interferences which will require additional sample preparations. All sample preparation details will be documented.

5.0 Safety

5.1 The toxicity or carcinogenicity of each chemical and reagent used in this method has not been precisely defined. However, each one must be treated as a potential health hazard, and exposure to these chemicals should be minimized. Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

5.2 Chemists working in the laboratory should follow ISWS safety rules :

5.2.1 A lab coat is required when working in the lab.

5.2.2 Eye protection with splash resistant safety glasses or safety goggles are required.

5.2.3 Protective gloves should be used while handling samples or standards. Special solvent resistant gloves should be used while handling large amount of solvents.

5.2.4 All solvent work should be done in fume hoods.

5.2.5 Open shoes are not allowed in the laboratory.

5.2.6 Particle mask is required when using dry silica.

5.2.7 Avoid working alone in the laboratory. If work must be performed after hours or in the weekend inform the supervisor or other staff so that your presence is known and will be accounted for in case of an emergency.

5.2.8 Chemicals and solvents are stored under the hoods. Acids must be separated from bases. A rubber bucket is required to transport any chemical.

5.2.9 Gas cylinders should be well secured at all times. Flammable gases are stored in separate storage areas.

5.2.10 Wash hands well after work.

5.2.11 No food or drink is allowed in the laboratory.

5.2.12 In case of minor spillage, get spillage kit to clean the area. A major spill requires the University of Illinois Fire Department to be contacted and the working area evacuated.

5.2.13 MSDS sheets are stored in the laboratory and a copy placed on file with the office administrator.

5.2.14 All chemicals and standards must be labeled with chemical name, date, and initials of person to contact.

5.2.15 Empty chemical bottles should be flushed out with water, or, in case of liquid, allowed to evaporate under a hood before discarding.

5.3 Waste Disposal

Solvents: Label waste containers, `*chlorinated waste*' and `*non-chlorinated waste*'. Glass bottles used for waste are placed under hoods for convenience. When full, transfer waste to 10 L carboy containers in solvent cabinet. Contact the ISWS Waste Coordinator for removal.

6.0 Equipment and Supplies

6.1 Glassware, General Requirements

All glassware, must be meticulously cleaned. Large glassware is thoroughly washed with laboratory detergent and hot water. Glassware with bad stains should be rinsed with MeOH or CH_2Cl_2 before using the soap and water procedure. If still not clean, soak in H_2SO_4:HNO_3 (50:50) acid bath overnight, then wash thoroughly with soap and water. Volumetric pipettes used for standards *must* soak in acid bath overnight. Glassware is thoroughly rinsed with tap water, then with DI water and allowed to air dry. The glassware is foil wrapped and heated 450°C for 4 hours. If glassware is not clean after muffling at 450°C for 4 hours, muffle at 500°C for 4 hours. The glassware is cooled to ambient temperature and stored in a clean location. Small glassware such as stoppers, vials, and disposables are wrapped in foil or placed into a beaker and covered with foil and heated to 450ºC for 4 hours, cooled to ambient temperature, and stored in a clean location. Vials are capped as soon as they are removed from the oven. Note: Always use dull side of foil towards glassware. Set initial temperature of furnace to 200ºC if possible.

6.2 Vortex Mixer

6.3 Volumetric flasks and pipets - Class A, various sizes

6.4 Autosampler vials, 2 mL, caps, teflon-lined septa, and 200 μL glass inserts.

6.5 Positive displacement micro pipet, glass capillaries (Drummond or equivalent)

6.6 GC-ECD (see section 11.0 for detailed information)

6.6.1 Hewlett-Packard 5890A capillary gas chromatograph with split/splitless capillary inlet, and electron capture detector (15 m Curie ^{63}Ni source)

6.6.2 Hewlett-Packard 3365 ChemStation, Version B.01.02

6.6.3 Autosampler: Hewlett-Packard 7673 or 7673A autosampler

6.6.4 Column:

For OC pesticides--30 m x 0.25 μm x 0.25 mm, DB-5 (J & W Scientific)

For PCBs--60 m x 0.1 μm x 0.25 mm, DB-5 (J & W Scientific)

6.7 J & W AccuRATE™, 1000 flowmeter (PN2201170, Folson, CA)

6.8 GL Sciences Inc.,LD223 flowmeter (Tokyo, Japan)

7.0 Reagents and Standards

7.1 All reagents will be pesticide residue quality or equivalent. All reagents are evaluated for interferences using laboratory blanks.

7.2 Solvents, EM Omnisolve or equivalent

7.2.1 Hexane

7.2.2 Methylene chloride

7.3 Standards

7.3.1 PCB and pesticide stock standards

Stock standard solutions are purchased from commercial sources (Ultra Scientific, Accustandard, Chem Service, Cresent Chemical), are obtained from the USEPA repository, or from the USEPA (PCB Mullin stock standard, 1994). When stock solutions are not available, analytes are purchased as the neat material and gravimetrically prepared in house. Stock solutions and mixed working standards are prepared volumetrically by serial dilution in volumetric flasks. A standards preparations are detailed in laboratory log books.

7.3.2 Chromatographic Calibration Standards

7.3.2.1 Mixed instrument calibration standards are prepared from the individual stock standards by volumetric dilution to obtain five concentration levels. The calibration standard concentrations bracket the expected analyte amounts in samples assayed and are within the working linear range of the detectors. Calibration mixes are prepared specifically for the appropriate instrument and fraction analyzed. Calibration mixes are described in "Standard Operating Procedure for the Analysis of PCBs, Pesticides, and PAHs in Air and Precipitation Samples," SOP #CH-PR-001.3, Revision 3.0, March 1995, Harlin and Surratt, ISWS, Champaign, IL 61820).

7.3.2.2 Standard Evaluation : New working standards will be assayed prior to use by comparison with existing standards. Standards must agree within 10% prior to use.

7.4 Gases

7.4.1 Hydrogen, carrier gas, 99.9995% chromatographic grade

7.4.2 Make-up gas, argon/methane (P5)

8.0 GC-ECD System Evaluation and Maintenance

8.1 System Evaluation

Before each run GC-ECD system performance and calibration are verified for all analytes. Hexane is injected at the beginning of each run to ensure the system is free from contaminants or interfering peaks. Records of daily system performance and maintenance are maintained.

8.1.1 Conditioning

A conditioning program is run prior to every analytical GC run with a hexane injection. The GC oven is set to 280°C, the injector at 280°C, and the ECD at 380°C for about half an hour (See Conditioning method, Appendix A; Method 1).

8.1.2 Injector

8.1.2.1 Septum: Prior to every analytical GC run the septum is changed. Prior to removing the septum the heated zones are cooled and the column oven cooled to 40°C.

Note: Many septa are rated to last for about 100 injections, however many are soft and small fragments frequently break off and enter the injection port or the split/splitless weldment. More frequent changes, such as before each run, help minimize this problem.

8.1.3 ECD Baseline Signal

The ECD baseline signal is usually below 30. After conditioning the system, hexane is analyzed at the start of every GC run to monitor the baseline stability. If the baseline signal is elevated or the hexane run produces a noisy chromatogram, the system should be evaluated for leaks or contamination.

8.1.4 Calibration standard performance

Inject a calibration standard to evaluate peak resolution, peak shape, and identification using the reference chromatograms in this SOP for evaluation. If the peak shapes are not satisfactory inspect the system for proper flow rates and leaks. If these are acceptable, remove 0.5-1 meter from the injector end of the column or install a new column.

8.1.4.1 PCBs: Over 90 peaks should resolved with congeners 77 and 110 separated from adjacent peaks. Monitor the ratio of the areas of the 30/204 ISTD peaks. This ratio will increase as the sensitivity for peaks in the later portion of the chromatogram are reduced (observe the peak area of congener 209). When this ratio exceeds 1.2 (a value of about 1 or less is desirable), the injection insert should be changed. In a run with a new injection insert, the peak area of 209 in a 595 ng/mL standard is easily seen. With repeated injections this peak area will decrease and can be used in addition to the 30/204 area ratio for determining the need for an injection liner change.

8.1.5 Leak checking and gas flows (See Appendix B for detailed instructions)
When the chromatography performance deteriorates check for gas leaks. Check around the septum, the injector connection, and at the detector connection of the column. Use of a leak detection fluid is discouraged because of the possibility of drawing the fluid into the system. A pure solvent such as isopropyl alcohol may be used as a leak detection fluid, however, an electronic leak detector is recommended such as the J & W AccuRATE™, 1000 flowmeter (PN2201170, Folson, CA)

Check the gas flow after any routine maintenance with a flowmeter. An electronic flowmeter is recommended such as the GL Sciences Inc., LD223 flowmeter (Tokyo, Japan).

8.2 Gases

Replace all tanks at 500 psig. Prior to changing a gas tank, lower GC oven temperature to 40° C for approximately 30 min. Maintain a 40°C oven temperature for approximately 30 min. after changing a tank to eliminate air from the system prior to heating the column and detector.

8.2.1 Carrier gas (hydrogen) flow rate.

The optimum carrier gas volumetric flow rate is specified by the column manufacturer. This is determined by measuring the time required for an unretained compound to elute from the column (such as methylene chloride vapor for an ECD), and then calculating the volumetric flow rate using the following formula:

$$\text{Volumetric flow rate (mL/min)} = \frac{\eth r^2 l}{t}$$

where:
ð is 3.14
r is the radius of the column (cm)
l is the length of the column (cm)
t is the retention time of the unretained compound (min)

8.2.2 Column head pressure should be at the preset value, usually 20/25 psi for 30/60 m columns. If the pressure is low, tighten the septum nut. If the pressure is still low check for leaks and tighten other connections.

9.0 Preparation of Autosampler Vials for GC-ECD Analysis

9.1 Initiate sample sequence table for the GC run. Each analytical run consists of a hexane blank, standard/s to establish a calibration table, a performance check standard (LPC), samples, a calibration check standard every 7-10 samples (if necessary), and a final calibration check (CLC).

9.2 Label autosampler vials for samples, standards, and hexane blanks; add inserts to vials.

9.3 Spike samples with ISTD if necessary (See Section 10.0 for spiking procedure).

9.4 Before transferring samples and standards to the corresponding labeled autosampler vials, mix contents of each vial and bottle well by holding on a vortex mixer for 5-10 seconds. Use muffled Pasteur pipettes for transfer.

10.0 ISTD Addition

10.1 Remove ISTDs from freezer; equilibrate to ambient temperature (approximately two hours). Vortex ISTD solution to mix.

10.2 Clean micropipette as follows: Remove glass capillary used to cover plunger. Rinse plunger with CH_2Cl_2 and allow to dry. Without manually touching glass capillaries, insert plunger into a new capillary, position and tighten. Rinse capillary in the following order: CH_2Cl_2, hexane (five times), air dry, ISTD solution (two times). Fill micropipette with the ISTD solution and dispense into sample vial.

10.3 Internal standard amount:

Fraction	Compound	ISTD	Spike Volume (μL)	Amount in Sample (ng)*	Color code
Hexane	PCBs and Pesticides	PCB 30	100	8	Red
		PCB 204		6	
40%	Pesticides	PCB 65	100	23.7	Blue
		PCB 155		17.5	
		DDE		20	
40%	PAHs	d10-Anthracene	100**	200	Black
		Triphenylmethane		100	
		d12-Benzo(a)anthracene		200	
		d12-Perylene		200	
MeOH	Atrazine	d10-Anthracene	100	200	Black

*Values in this column are approximate and may change slightly depending on the exact concentrations of the compounds in the stock solutions.
**If the sample is expected to be high in concentration of PAHs or if the final sample volume is greater than 2 mL, more ISTD solution may be added in increments of 100μL.

10.4 Mark each sample vial label with the appropriate color code verify ISTD addition with a water-proof marker.

10.5 Rinse the micropipette with solvent and replace glass capillary used to cover plunger.

10.6 Label the sample set with the following information (using the same color code as dots on vial labels):
Date sample vials spiked.
Fraction spiked.
Initials of chemist spiking.

11.0 GC-ECD Analytical Run Conditions

11.1 Initial Check

Ensure sufficient carrier (hydrogen) and make-up gas (argon/methane, P5) to complete the run. Change the septum as described in 8.0. Change the solvent in the autosampler wash vials.

11.2 ChemStation Control

The ChemStation software controls the GC. Analyzer 1 controls GC1 and Analyzer 2 controls GC2. Load the analysis method. "MULLIN.MTH" for PCBs and "ISWS'PES.MTH" for OC pesticides. Verify method parameters are correct. Edit the method if changes are necessary and resave the method. Copies of these methods are included in Appendix A- Method 2 or Method 3.

11.3 Load the method sequence. "ISWS'PCB.SEQ" for PCBs and "ISWS'PEST.SEQ" for OC pesticides. Edit the sequence *parameters* to include:

operator's name
subdirectory name
calibration standard information
spike target levels
final sample volume
sample batch code
comments

In the *sequence table* ensure the correct injector is selected (rear vs front) and enter the "from vial" and "to vial" numbers for selected methods. The first hexane injection will utilize the "BAKE.MTH" method to condition the system.

Edit the sequence *sample table* to enter sample ID numbers (the ID#=sample name with a ", hex" or ", 40" suffix to indicate the hexane or 40%DCM fraction respectively). Hexane is always the first vial followed by two vials of the calibration standard, a calibration performance check (LPC). Samples usually begin with the 5th vial. Each sample batch will include a hexane blank, a calibration standard, a LPC, and an end of run calibration check.

Verify the correct method name is entered in the *sample log table* and the multiplier is entered for each sample (usually 1). Verify the start and end vial numbers. Save the method and sequence on disk using the path for the directory created for this sample batch. Print copies of the sequence for the sequence log and the raw data file for the sample batch. An example of a PCB sequence is shown in Appendix C.

11.4 GC Conditions, typical run conditions are listed below.

PCBs:

Oven Program: 158 minutes

Initial temperature: 100°C

Ramp 1: 1°C/min. to 235°C

Ramp 2: 15°C/min. to 280°C, hold 20 min.

Injector temp. 250°C

ECD: 350°C

OC pesticides:

Oven Program: 147 minutes

Initial temperature: 70°C, hold 1 min.

Ramp 1: 5°C/min. to 140°C

Ramp 2: 0.2°C/min. to 160°C .

Ramp 3: 10°C/min. to 280°C, hold 20 min.

Injector temperature 250°C

ECD: 350°C

11.5 Calibration

A multipoint calibration curve is prepared yearly for each analyte to document the linear range. A single point calibration standard is injected in duplicate immediately prior to a sample run. Compare the duplicate injections of the calibration standard to ensure the system has stabilized and is reproducible. Inject a calibration performance standard (LPC) immediately after the calibration standard. The acceptable ranges for the LPC are defined in the QAPjP for the project. Inject a calibration standard every 5-10 samples (for multi-batch runs) and at the end of each run. Recalibration is required if a shift of >20% is observed for OC pesticides and >25% for congeners 1, 6, 29, 49, 101, 141, 180, 194, 206, and 209 for PCBs. The methods of internal standard calibration is utilized. The chromatogram is divided into two time segments with each segment calibrated relative to one internal standard response for the PCB runs.

12.0 Data Reduction

12.1 Data Files

The electronic data are converted to compacted (zipped) format for storage and transfer to other computers for data reduction.

12.2 Chromatogram and ISTD report

The data files are expanded (unzipped) and the appropriate method (*.MTH) and data files loaded to view the chromatogram, generate calibration tables, and ISTD reports. Each analyte peak is evaluated for proper peak integration, baseline correction, and peak identification. The final integrated data and all associated files are saved on removable disks. The chromatograms and ISTD reports are also printed as hard copy reports and compiled as a sample batch data file (filed by the GC sequence name). The hard copy files are initialed by the data analyst. PCB and OC pesticide macro programs convert the ChemStation data into a spreadsheet format for further data storage and retrieval. All data are reviewed by the laboratory supervisor prior to release.

A properly integrated and identified chromatograms for a 595 ng/mL PCB standard and a 20 ng/mL OC pesticide standard are presented in Appendix C. Calibration tables and sample data are included.

12.3 Data Storage

All chromatography data are archived including: ChemStation raw data files, processed data files, and associated calibration and integration files along with associated spreadsheet files. These files are stored on 5.25" and 3.5" data disks and are filed by the GC sequence name. Duplicate copies of the raw data disks are stored in two separate buildings.

Appendix A. GC Methods

METHOD 1- System Conditioning

Injector Information

Injection Source:	Auto
Injection Location:	Dual

Front:

Sample Washes:	3
Sample Pumps:	5
Sample Volume:	1 stop
Viscosity Delay:	0 sec.
Solvent A Washes:	6
Solvent B Washes:	6
On-Column:	No

Rear:

Sample Washes:	3
Sample Pumps:	5
Sample Volume:	1 stop
Viscosity Delay:	0 sec.
Solvent A Washes:	6
Solvent B Washes:	6
On-Column:	No

Purge A/B:

	Init Value	On Time (Min.)	Off Time (Min.)
A (Valve 3)	On	0.00	40.00
A (Valve 4)	On	0.00	40.00

Temperature Information

Zone Temperatures:

	Set Point
Inl. A	280 C.
Inl. B	280 C.
Det. A	380 C.
Det. B	380 C.

Oven Parameters:

Oven Equib. Time:	1.00 Min.
Oven Max:	300 C.
Oven	On
Cryo	Off

Appendix A. GC Methods (Cont'd)

METHOD 1 (Cont'd)

Oven Program:

	Set Point
Initial Temp:	280 C.
Initial Time:	20.00 Min.

Level	Rate (C./Min.)	Final Temp. (C.)	Final Time. (Min.)
1	0.00		
2 (A)			
3 (B)			
Next Run Time:	20.00 Min.		

Signal Information

Save Data:	Both
Signal 1	
Source:	Det. A
Peak Width:	0.053 Min.
Data Rate:	5.000 Hz.
Data Storage:	All
Signal 2	
Source:	Det. B
Peak Width:	0.053 Min.
Data Rate:	5.000 Hz
Data Storage:	All

Detector Information

Detector	Type	State
A	ECD	On
B	ECD	On

Signal Plot Information

Signal	Attn. (2^)	Offset (%)	Time (Min.)
1	2	20	20
2	2	20	20

Appendix A. GC Methods (Cont'd)

METHOD 2- PCBs

Method Information

This method is for IL H2O Survey.

Run Time Checklist

Pre-Run Program:	None
Name:	
Parameter:	
Data Acquistion:	On
Data Analysis:	On
Sig. 2 Mth:	None
Post-Run Program:	None
Name:	
Parameter:	

Injector Information

Injection Source:	Auto
Injection Location:	Dual

Front:

Sample Washes:	3
Sample Pumps:	5
Sample Volume:	2 stops
Viscosity Delay:	0 sec.
Solvent A Washes:	6
Solvent B Washes:	6
On-Column:	No

Rear:

Sample Washes:	3
Sample Pumps:	5
Sample Volume:	2 stops
Viscosity Delay:	0 sec.
Solvent A Washes:	6
Solvent B Washes:	6
On-Column:	No

Appendix A. GC Methods (Cont'd)

METHOD 2 (Cont'd)

Purge A/B:

	Init Value	On Time (Min.)	Off Time (Min.)
A (Valve 3)	On	0.00	40.00
A (Valve 4)	On	0.00	40.00

Temperature Information

Zone Temperatures:

	Set Point
Inl. A	250 C.
Inl. B	250 C.
Det. A	350 C.
Det. B	350 C.

Oven Parameters:

Oven Equib. Time:	3.00 Min.
Oven Max:	280 C.
Oven	On
Cryo	Off

Oven Program:

	Set Point
Initial Temp:	100 C.
Initial Time:	0.00 Min.

Level	Rate (C./Min.)	Final Temp. (C.)	Final Time. (Min.)
1	1.00	235	0.00
2 (A)	15.0	280	20.0
3 (B)	0.00		

Next Run Time: 158.00 Min.

Signal Information

Save Data: Both

Signal 1

Source:	Det. A
Peak Width:	0.053 Min.
Data Rate:	5.000 Hz.
Data Storage:	All

Appendix A. GC Methods (Cont'd)

METHOD 2 (Cont'd)

Signal 2

Source:	Det. B
Peak Width:	0.053 Min.
Data Rate:	5.000 Hz
Data Storage:	All

Detector Information

Detector	Type	State
A	ECD	On
B	ECD	On

Sequence Recalibration Table

Cal. Line	Cal. Level	Update Response Factor	Update Retention Times	Recalib Interval

Signal Plot Information

Signal	Attn. (2^)	Offset (%)	Time (Min.)
1	2	20	20
2	2	20	20

Appendix A. GC Methods (Cont'd)

METHOD 3- OC Pesticides

Method Information

This method is for IL H_2O Survey.

Run Time Checklist

Pre-Run Program:	None
Name:	
Parameter:	
Data Acquistion:	On
Data Analysis:	On
Sig. 2 Mth:	None
Post-Run Program:	None
Name:	
Parameter:	

Injector Information

Injection Source:	Auto
Injection Location:	Dual

Front:

Sample Washes:	3
Sample Pumps:	5
Sample Volume:	1 stop
Viscosity Delay:	0 sec.
Solvent A Washes:	6
Solvent B Washes:	6
On-Column:	No

Rear:

Sample Washes:	3
Sample Pumps:	5
Sample Volume:	1 stop
Viscosity Delay:	0 sec.
Solvent A Washes:	6
Solvent B Washes:	6
On-Column:	No

Appendix A. GC Methods (Cont'd)

METHOD 3 (Cont'd)

Purge A/B:

	Init Value	On Time (Min.)	Off Time (Min.)
A (Valve 3)	Off	0.50	140.00
A (Valve 4)	Off	0.50	140.00

Temperature Information

Zone Temperatures:

	Set Point
Inl. A	250 C.
Inl. B	250 C.
Det. A	350 C.
Det. B	350 C.

Oven Parameters:

Oven Equib. Time:	1.00 Min.
Oven Max:	300 C.
Oven	On
Cryo	Off

Oven Program:

	Set Point
Initial Temp:	70 C.
Initial Time:	1.00 Min

Level	Rate (C./Min.)	Final Temp. (C.)	Final Time. (Min.)
1	5.00	140	0.00
2 (A)	0.20	160	0.00
3 (B)	10.0	280	20.0

Next Run Time: 147.00 Min.

Signal Information

Save Data: Both

Signal 1

Source:	Det. A
Peak Width:	0.053 Min.
Data Rate:	5.000 Hz.
Data Storage:	All

Appendix A. GC Methods (Cont'd)

METHOD 3 (Cont'd)

Signal 2

Source:	Det. B
Peak Width:	0.053 Min.
Data Rate:	5.000 Hz
Data Storage:	All

Detector Information

Detector	Type	State
A	ECD	On
B	ECD	On

Sequence Recalibration Table

Cal. Line	Cal. Level	Update Response Factor	Update Retention Times	Recalib Interval

Signal Plot Information

Signal	Attn. (2^)	Offset (%)	Time (Min.)
1	2	20	20
2	2	20	20

Appendix B. GC-ECD Maintenance

B.1 Injection Port Cleaning and Liner Installation

B.1.1 Turn oven, injector and detector off

B.1.2 After everything cools, turn hydrogen off

B.1.3 Remove autosampler towers

B.1.4 Remove the septum retainer nut and the split/splitless weldment (the large nut underneath the septum) to expose the injection liner. Remove the liner

B.1.5 Open the oven and disconnect the column from injector end of the GC. The open end of the column should not be exposed to air so plug the open end with a septum

B.1.6 Unscrew the reducing nut (inside the oven, below the injection liner). There is one gold seal and a washer in it. Washer and seal need to be replaced each time it is taken apart

B.1.7 Put a beaker inside the oven underneath the injection port and rinse the injector with hexane. Clean the injection port with Q-tips and rinse again with hexane

B.1.8 Check inside the split/splitless weldment, below where the septum sits. Some septa particles may be inside. Complete removal may be impossible, however some particles may be removed using a small tool similar to a dental tool. Also washing hexane through the opening with a Pasteur pipet helps, being careful not to break pipet tips off inside this cavity

B.1.9 Place a new washer followed by a new gold seal in the reducing nut. The tapered opening of the seal will face downward (the tapered end will be fitted to the ferrule from the column). Tighten this reducing nut before placing the injection liner in the injection port

B.1.10 Insert a new liner. Some liners are not symmetrical but require a specific orientation. Take care to insert properly

B.1.11 Place a viton O- ring (rated for the injector temperature range) on the liner. Put the split splitless weldment (big nut) on and tighten it. Install in a new septum. Replace and tighten the septum nut

B.2 Column Installation

B.2.1 Remove the column from the injector end. Remove the ferrule and all particles from the column nut. Before removing a section of the column, insert a clean column nut onto the column, followed by a new ferrule, with conical end pointing towards the open end of the column (small pieces of ferrule material can get inside the column, therefore, a new section of column must be exposed after the ferrule is on).

Appendix B. GC-ECD Maintenance (Cont'd)

B.2.2 Cut off the injector end of the column. Remove 0.5-1 meter from an existing column. For a new column, remove a few inches. Make a clean cut with diamond tip score or ceramic wafer. Examine the cut under a magnifier to ensure it is square

B.2.3 Measure 23 mm from the tip of the column. Mark this point with Liquid Paper®. Before marking, the ferrule should be between the end of the column and the 23 mm point

B.2.4 Carefully insert the column, fitted with nut and ferrule, through the reducing nut into the injection port. Insert column far enough that the white mark is at least even with the end of the column nut, or a little further in so that white mark is up inside column nut, and tighten slightly. As soon as the ferrule starts gripping the column, pull the column out gently just until the white mark is seen. Hand tighten column nut then turn at least ¼ additional turn

B.2.5 Detector end of the column (if needed): Remove the column from the detector end. If a portion of the ferrule is stuck inside the makeup gas adaptor remove by turning a threaded tool (such as a small file) into the ferrule and pulling it out. The makeup gas adaptor may need to be removed to remove the ferrule. When replacing the makeup gas adaptor, a 1/4 inch vespel ferrule is used. Place a column nut and ferrule on the column in the same way as described for the injector end. Remove a portion of the column and check for cut as described above. Measure 70 mm from the end of the column and put a white mark on the column, place the ferrule between the end of the column and the 70 mm point before marking. Turn hydrogen on and check the flow of gas through the column by inserting the cut end in a beaker of hexane. Turn hydrogen off

B.2.6 Carefully fit the column into the detector, slightly tighten the column nut and pull the column out until you see the white mark. Tighten with wrench ¼ turn after hand tight.

B.3 Leak Checking and Gas Flow Measurement

B.3.1 Turn hydrogen and argon/methane on. Check leaks with a leak detector . An electronic leak detector is recommended such as the J & W AccuRATE™, 1000 flowmeter (PN2201170, Folson, CA). Check around the septum, and at the injector and at the detector end of the column. Check the column head pressure for the appropriate reading

B.3.2 Check the gas flow with a flowmeter. An electronic flowmeter is recommended such as the GL Sciences Inc.,LD223 flowmeter (Tokyo, Japan).Approximate gas flow in both GCs are as follows :

Split vent	130 mL/min
Purge vent	2 mL/min.
Total flow through detector	22 mL/min

Appendix B. GC-ECD Maintenance (Cont'd)

B.4 Reassembly

B.4.1 Replace autosampler towers

B.4.2 Turn heated zones on

B.4.3 If injector was allowed to cool, retighten the septum retainer nut to avoid a leak at that point

B.4.4 Turn oven on and set to 40°C for about an hour; then increase oven temperature to 70°C for an hour.

B.4.5 If a used column, bake the column, injector and detector until baseline stabilizes. If the baseline has not stabilized within an hour, other problems probably require identification and correction.

B.5 System conditioning

B.5.1 Set the temperature setting to the following (see Appendix A for GC method):

Oven: 280°C
Injector A: 280°C
Injector B: 280°C
Detector A: 380°C
Detector B: 380°C

B.5.2 Run approx. 6 hexane blanks by the instrumental method being evaluated

B.5.3 If a new column, bake injector and detector by ramping oven temp 1-2°/min. to 280°C and hold there for 1 hour. After conditioning, run 6 hexane blanks by the method being evaluated

B.5.4 If the hexane blank runs look satisfactory, evaluate a calibration standard before resuming analysis of samples.